

Phosphorus and Greenhouse Gas Dynamics in a Drained Calcareous Wetland Soil in Minnesota

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Restoration of wetland hydrology can produce ecological benefits but may have unintended consequences. We examined effects of altered water level on release of dissolved reactive phosphorus (DRP) and greenhouse gases (GHG) in soil cores from a marsh being evaluated for restoration. We also measured field concentrations of DRP and other constituents in wetland porewater. Intact cores from a sampling location with higher Fe and lower calcium carbonate (CaCO_3) contents released more DRP than another location, and displayed higher DRP under completely saturated compared to partly drained conditions. Porewater samples collected from the high-Fe location also contained higher DRP levels. Chemical data suggest that redox-driven reactions largely controlled DRP levels at the high-Fe site, while CaCO_3 adsorption was more important at the low-Fe site. Over the long term, water table elevation may attenuate P draining from the wetland due to decreased mineralization. However, such measures may increase P release in the short term. Raising the water level in soil cores resulted in decreased nitrous oxide (N_2O) emissions, increased methane (CH_4) emissions, and an overall increase in total global warming potential (GWP). The proportion of total GWP contributed by N_2O decreased from 14% to $\leq 1\%$ as water level was raised, while the proportion contributed by CH_4 increased from 10 to 20% to 60 to 80%. Restoration of hydrology in the Rice Lake wetland has the potential to affect both local water quality and global air quality. These combined effects complicate the cost-to-benefit analysis of such wetland restoration efforts.

FROM 1780 to 1980, wetland acreage in the United States declined by approximately 30%, largely through drainage to provide for agriculture (Dahl and Pywell, 1989). More recently, increased recognition of wetland benefits has shifted policy toward preservation and restoration, resulting in an increase of wetland area in the United States by approximately 13,000 ha yr⁻¹ during 1998 through 2004 (Bardecki, 1984; Dahl, 2006). Alteration of wetland hydrology necessary for restoration can affect soil nutrient cycling with potentially negative environmental impacts due to the release of nutrients, including P, and the emission of GHG including methane (CH_4) (Shenker et al., 2005; Moore and Knowles, 1989).

A major mechanism for P retention and release in saturated agricultural soils is through oxidation and reduction of Fe–P complexes (Patrick and Khalid, 1974). Studies of Fe–P relationships have since been extended to natural or amended wetland soils (Moore and Reddy, 1994; Saleque et al., 1996; Olila and Reddy, 1997). These studies demonstrated that sorption and release from Fe oxyhydroxides and calcium carbonate driven by changes in soil pH and oxidation–reduction potential (Eh) largely explain P release in flooded soils. Cycling of P in wetland soils is also influenced by mineralization of organic matter, which may occur under both aerobic and anaerobic conditions (Bridgman et al., 1998). Because of the multiple mechanisms that can result in net P release from wetland soils, it is difficult to predict how altering the hydrology in a specific wetland will impact downstream water quality.

Emissions of GHGs can also respond to changes in wetland hydrology, although the direction of change and resulting impact may vary and depend on the particular gas. It has been repeatedly demonstrated that raising water levels or flooding will increase soil-to-atmosphere CH_4 fluxes (Moosavi et al., 1996; Fiedler and Sommer, 2000; DeBusk and Reddy, 2001; Freeman et al., 2002). The existence of multiple controls over nitrous oxide (N_2O) production in soil makes it difficult to predict the effects of hydrolog-

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Abbreviations: DOC, dissolved organic carbon; DRP, dissolved reactive phosphorus; GHG, greenhouse gas; GWP, global warming potential.

ic alterations on net N_2O emissions for any particular wetland. Production of N_2O from microbial reduction of nitrate (NO_3^-) (i.e., denitrification) increases under wetter and more anaerobic conditions (Firestone and Davidson, 1989). However, in highly reduced environments, it is possible that further reduction of N_2O to N_2 may limit the amount of N_2O that is released at the soil surface (Venterea, 2007). Prolonged anaerobic conditions, in the absence of external inputs of NO_3^- , may also limit N_2O production due to limited nitrification (Freeman et al., 1997). Few studies have examined the impacts of altered wetland hydrology on the sum of carbon dioxide (CO_2), N_2O , and CH_4 emissions, or examined the simultaneous effects of hydrologic factors on the release of P and GHGs.

The current study was conducted in a wetland created by artificial drainage of a shallow lake (Rice Lake) in northwestern Minnesota, which drains into a popular recreational lake (Detroit Lake). The mean total and DRP concentrations at the wetland outlet during 1998 to 2000 were 95 and 52 $\mu\text{g L}^{-1}$, respectively, which exceed water quality criteria of 30 $\mu\text{g L}^{-1}$ for swimmable waters in this region (NRCS, 2007). To protect water quality in Detroit Lake, it was proposed that restoration of the wetland's preditched hydrology would reduce P mineralization, eliminate transport of P-laden porewater, and increase retention time of runoff within the wetland (NRCS, 2007). Therefore, one objective of this study was to examine the effects of simulated water level elevation on both P release and GHG emissions using intact soil cores from the Rice Lake wetland. We also used in situ porewater sampling to examine spatial and temporal dynamics of porewater P under current conditions over two consecutive growing seasons.

Materials and Methods

Site Description

The Rice Lake Wetland is located near the city of Detroit Lakes, Minnesota (46°51' N, 95°49' W) (Fig. 1). Air temperatures range from mean lows of -16.7°C in January to mean highs of 28.6°C in July. Mean annual precipitation during 2000 to 2004 was 705 mm, with June having the highest monthly average (126 mm). The 105-ha wetland was formerly a larger, deeper wetland in a glacial outwash plain formed in calcareous till that was drained in 1913 by means of a hand-dug canal ("Ditch 13") to make the land suitable for agriculture. The ditch drains from north to south into the upper branch of the Pelican River which discharges to Detroit Lake (1250 ha). Records indicate that extensive pasturing occurred within the wetland during the dry years of the 1930s. However, after the drought years, much of the wetland hydrology returned and the area was abandoned for agricultural use. The remnant ditch remains, leaving the wetland in a semi-drained state, and making it difficult to access large interior areas of the wetland. The wetland has evolved into a shallow marsh dominated by cattail (*Typha* spp.) vegetation, with uniform cattail cover (> 90%) across all sampling locations used in the current study. Following water quality assessments by local, state, and federal agencies conducted during 1998 to 2004, it was hypothesized

that the original ditching through the wetland was accelerating P release from the organic materials by enhancing oxidation due to increased aeration in the upper soil layers during the summer. Soils are mapped as Nidaros series (loamy, mixed, euic, frigid Terric Haplosaprists, USDA soil classification) and Haslie series (coprogenous, euic, Limnic Haplosaprists, USDA soil classification), though soils used in the study resemble Nidaros more than Haslie. Total and Olsen P levels are highest in soil from the northern edge of the wetland (North site, Fig. 1, Table 1), which also has higher Fe and organic matter content than soils from the other samples sites.

Soil Column Experiments

Intact soil cores were collected at the South and North sites (Fig. 1) in March 2004 and March 2005, respectively, using a hollow auger designed to collect frozen soil (Rand and Mellor, 1985). Each sample consisted of a 76-mm diam. frozen core extending from the surface to the frost depth. Samples were sealed at both ends and stored at -5°C in polyvinyl chloride (PVC) tubes. Nine cores from each location were cut while frozen and randomly assigned to a High (+15 mm relative to soil surface), Intermediate (-75 mm), or Low (-150 cm) water level treatment ($n = 3$ for each water level) (Fig. 2a). Total column lengths were determined by the minimum depth of the frost layer at the time of sampling (0.26 and 0.17 m for cores from the South and North sites, respectively). Three additional cores collected from the North site were removed from the original tubes and cut into three depth intervals (0–0.1, 0.1–0.2, and 0.2–0.3 m). The cut sections were allowed to thaw for 24 h to generate liquid porewater for analysis of initial $\text{NO}_3^- + \text{NO}_2^-$ concentrations using a flow-through injection analyzer (Lachat, Milwaukee, WI).

After cutting, cores were transferred to separate 76-mm id PVC tubes that served as experimental columns. Each column was sealed on the bottom with a PVC cap, fitted along one side with ports for placement of porewater samplers, and on the opposite side with ports for placement of oxidation–reduction potential (Eh) electrodes (Fig. 2a). Cylindrical bosses with 12-mm holes bored through their centers extended from the outer surface of the column at each side-port location to facilitate securing porewater samplers and Eh electrodes. Holes were drilled into the frozen soil through the side-ports for initial installation of porewater samplers and Eh probes.

In each column, a "Bottom" porewater sampler was placed 10 mm from the lower end of the column, and a "Top" sampler was placed 5 mm below the free water surface (Fig. 2a). Each porewater sampler consisted of a 30-mm long \times 10-mm diam. stainless steel (SS) cylinder with pore size rated at 20 μm (Mott Corp., Farmington, CT). The cylinders were soldered to 3-mm i.d. threaded SS tubes which in turn were connected to flexible plastic tubing. Toggle valves fitted to the tubing were kept closed except when withdrawing samples. On the opposite side of each column, three combination Eh electrodes (Cole Parmer, Vernon Hills, IL) were inserted at 50- to 80-mm intervals and sealed with rubber O-rings. Data from the Eh probes were recorded at 30-s intervals (CR 21X, Campbell Scientific, Lo-

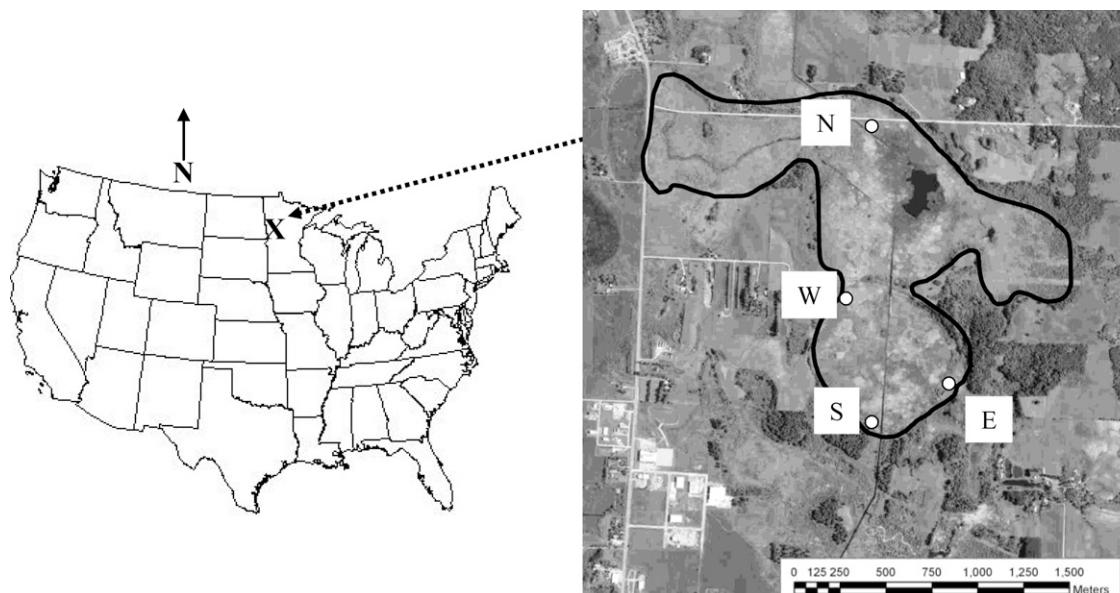


Fig. 1. Location of Rice Lake wetland and sampling sites. Porewater equilibrators were deployed at the North (N), South (S), West (W), and East (E) sites. Soil cores for laboratory column experiments were collected at the N and S sites.

Table 1. Selected properties of wetland soils (0–0.15 m depth).

Site	Bulk density	pH	OM†	CCE‡	Ca§	Mg	Mn	Fe	Total P	Olsen P#
	g cm^{-3}	1:1 soil/water			g kg^{-1}					mg kg^{-1}
North	0.24	7.6	468	143	80.0	4.4	0.59	13.4	0.96	16
South	0.66	7.7	238	557	209	6.6	0.71	9.9	0.36	6
East	0.52	7.5	280				not determined			
West	0.67	7.6	250							

† Organic matter (OM) was determined by loss-on-ignition.

‡ Calcium carbonate equivalent (CCE) was calculated from total inorganic carbon content which was determined by treatment with phosphoric acid followed by IR-spectrum measurement of CO_2 evolution.

§ Ca, Mg, Fe, and total P were determined in air-dried samples using inductively coupled plasma spectroscopy.

Olsen extractable phosphorus was determined after extraction in NaHCO_3 at pH 8.5.

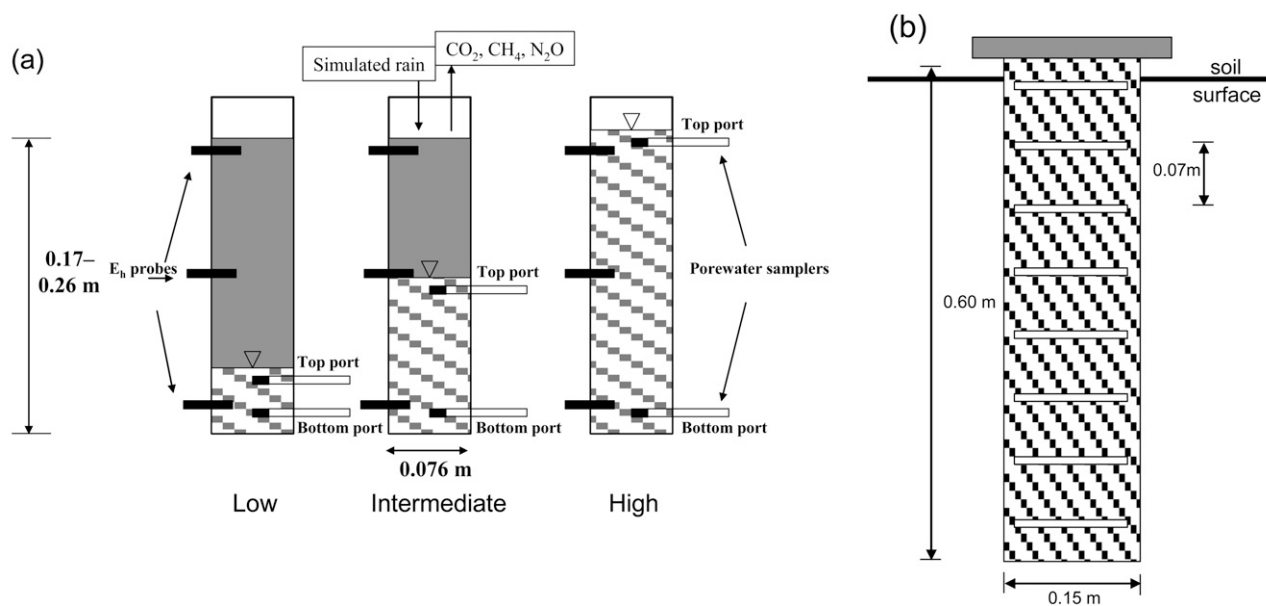


Fig. 2. Schematics of devices used for (a) soil column experiments, and (b) in situ porewater sampling. In (a) water level is indicated by an upside down triangle, and in each column, a "Bottom" porewater sampling port was located 0.10 m from the bottom, and a "Top" port was located 0.05 m below the water surface.

gan, UT). Resistors (10 Mohms) were used in the multiplexer to stabilize Eh readings (van Bochove et al., 2002). The means of 30-s readings were determined every 10 min, and hourly averages of 10-min means were used for data analysis. Mean values obtained from the Top and Middle Eh ports, and from the Bottom and Middle Eh ports, respectively, were used for comparison to chemical parameters measured in water samples collected from the Top and Bottom water sampling ports.

Water levels were initially established by draining water through transparent plastic tubing attached to a hole in the bottom cap and placing the free end of the tubing at the desired height. The tubing was sealed with a metal clamp and used to monitor the water level during the experiment. Soil columns were incubated in a dark growth chamber at 20°C and >95% relative humidity. Because we expected that, during thawing, microbial activity would be greatly stimulated by the dissolved organic matter produced while freezing, soil columns were acclimated for 1 wk before sampling. Thawing is an annual process in this wetland's soil; we wanted to allow the microbial community some time to metabolize the fresh inputs without allowing too much time to pass before beginning our sampling regime. Columns were kept open to air except during gas flux sampling (described below). To simulate rainfall events and maintain water levels, a dilute salt solution was applied as a fine mist on the surface of each column before porewater sampling. Total water volume removed in the subsequent sampling was roughly equivalent to the volume of solution added. Small, unavoidable evaporative losses required occasional minor adjustments to maintain water levels. The solution was designed to represent average rainfall composition derived from the averaging of three recording sites (ND11, Woodworth; ND08, Icelandic State Park; and MN23, Camp Riley) and contained (in mg L⁻¹): 0.238 Ca²⁺, 0.047 Mg²⁺, 0.035 K⁺, 0.035 Na⁺, 1.466 (NH₄⁺ plus NO₃⁻), 0.065 Cl⁻, 0.895 SO₄²⁻ (National Atmospheric Deposition Program, 2004). Porewater samples were withdrawn from the Top port (sampled first) and the Bottom port using a polypropylene syringe connected to the tubing.

Water addition and sampling schedules for column experiments conducted with soil cores from the South and North sites are shown in Table 2. In the first experiment (using soil from the South site), moderate water inputs (~8–16 mm wk⁻¹) were applied at regular intervals for the entire experiment. The second experiment (using soil from the North site) was designed to examine the effects of larger rainfall events (~20 mm) alternating with drier periods lasting 3 wks with additions of ~2 mm wk⁻¹. At the conclusion of the first 10 wk (referred to hereafter as “Phase I”), the water level in the Low water level treatment (–150 mm) was raised to that of the High water level treatment (+15 mm). The Phase II manipulation was designed to examine the effects of complete saturation after a prolonged period of partial drainage.

Immediately following porewater collection, 1-mL subsamples were passed through 0.2-μm polyethersulfone syringe filters, and 0.3 mL of this was immediately reacted with phenanthroline reagent for dissolved iron (Fe²⁺) determina-

tion (APHA et al., 1998). Porewater subsamples (2–3 mL) were passed through 0.2-μm polyethersulfone syringe filters, acidified with HCl, and stored at 4°C for subsequent analysis of DRP using the ascorbic acid method (Murphy and Riley, 1962), which was performed within 2 wk of collection. Separate subsamples (~2 mL) were taken for pH analysis, which was performed immediately using a portable pH meter (Thermo, Waltham, MA). For all samplings from the South site columns and following the two larger water inputs to the North site columns (Table 2), additional subsamples were frozen for subsequent analysis of dissolved organic carbon (DOC) by UV-persulfate oxidation (Phoenix 8000, Tekmar-Dohrmann, Cincinnati, OH). Samples collected on Day 57 in the North site experiment were also analyzed for nitrate concentration.

Fluxes of CO₂, CH₄, and N₂O were measured by securing a PVC cap fitted with a septum sampling valve to the top of each column for 1 h. A needle was inserted into the septum while securing the cap to minimize pressure disturbances. Gas samples (12 mL) were removed immediately and then after 30 and 60 min using a polypropylene syringe. Samples were immediately transferred to 9-mL glass vials fitted with butyl rubber septa, and analyzed within 1 wk by gas chromatography (GC). Two GCs (Agilent/Hewlett-Packard, Palo Alto, CA), one equipped with a thermal conductivity detector for CO₂ and an electron capture detector for N₂O, and the other equipped with a flame ionization detector for CH₄, were connected to a headspace autosampler (Teledyne Tekmar, Mason, OH). Each sample was split into three separate sample loops using a 14-port valve (Valco Instruments, Houston, TX). Gas fluxes were calculated from the rate of change in gas concentration, the headspace volume for each soil column (approximately 0.0003 m³), and soil surface area (0.0046 m²). The detectors were calibrated daily using certified gas standards (Scott Specialty Gases, Plumsteadville, PA). Greenhouse gas fluxes were measured at approximately 6-d intervals in the South site column experiment and 1 d before and 1 d following each water sampling (during Phase I only) in the North site experiment.

Field Porewater Sampling

In situ porewater equilibration samplers based on the concept of Hesslein (1976) with refinements by Suplee and Cotner (2002) were used to collect porewater from the wetland. Each sampler consisted of a PVC plate (0.60 m high × 0.15 m wide × 25 mm thick) into which eight slots (10 by 135 mm) were bored at 0.7-m intervals (Fig. 2b). The samplers were inserted into the soil so that the sample tubes were positioned at depths of 0, 0.07, 0.14, 0.21, 0.28, 0.35, 0.42, and 0.49 m relative to the soil surface. Before deployment, polytetra-fluoroethylene (PTFE) sample tubes containing 8 mL of deionized water were placed into each slot. Each sample tube had a 95 by 12.5 mm window cut in one side which was covered by a 0.45-μm polyethersulfone membrane that allowed solutes in the surrounding porewater to diffuse into the tubes. In 2004, five samplers were positioned at 7-m intervals along transects perpendicular to Ditch 13 at each of the N and S locations. In 2005, three samplers were similarly deployed at the E and W locations in addition to five samplers at the N and S sites. Before each deployment, samplers were sub-

Table 2. Schedule of water addition and sample collection in column experiments using soil cores collected from the South and North sites.

Week	Frequency		Volume†	
	Addition	Sampling		
	time per wk		mL	mm‡
South				
1–2	2	2	36	7.9
3–7	1	1	36	7.9
North (Phase I)				
1–3		1	10	2.2
4		4§	90	19.7
5–7	1	1	10	2.2
8		1#	90	19.7
9–10		1	10	2.2
North (Phase II)				
11–24	0.5††	0.5††	10	2.2

† Volume of water added at each event. An equivalent volume of sample was collected within 1 h after each addition, except in Weeks 4 and 8 of the North experiment.

‡ Actual units are mm³ H₂O mm⁻² soil.

§ In Week 4, 22.5-mL samples were taken 1, 3, 5, and 7 d after adding 90 mL.

In Week 8, a 90-mL sample was taken 7 d after adding 90 mL.

†† Water was added and samples were collected once every 2 wk during Phase II.

merged in deionized water and purged with dinitrogen (N₂) for 24 h to remove dissolved oxygen. At 2-wk intervals, samplers were removed from the field and replaced with freshly-purged samplers. A portion of the contents of each tube was immediately taken for pH analysis (during 2004 only). The remaining contents were transferred to glass vials and amended with HCl to a pH of about 1 and analyzed for DRP within 14 d. Total dissolved metals, including Ca, Fe, K, Mg, Mn, and Na were also determined using inductively coupled plasma spectrometry (ICP) for samples collected during August 2004.

Water table level was monitored weekly from shallow piezometers installed at the North and South sites (one per site). Piezometers were constructed from 0.076 m diam. PVC tubing with holes drilled into the entire length and covered in landscaping fabric, and they were installed according to ERDC guidelines (Sprecher, 2000).

Data Analysis and Statistics

Differences in DRP and soluble iron concentrations in samples collected from each sampling port during the soil column experiments were evaluated using ANOVA appropriate to a split-plot design with water table level as the main effect and sampling date as the subplot effect. Means among different treatments were compared using least significant differences (LSD), which were calculated manually using error mean squares obtained by ANOVA or GLM procedures in SAS (SAS Institute, 2001) and critical *t* values (Gomez and Gomez, 1984). Fluxes of N₂O and CH₄ were converted to GHG units (CO₂ equivalents) using 100-yr horizon GWP for N₂O and CH₄ (Forster et al., 2007). Total GHG emissions from each column were estimated by trapezoidal integration assuming that measured fluxes represented mean daily fluxes and that mean daily fluxes changed linearly between measurements. Regression analysis was conducted to examine relationships be-

tween chemical parameters (pH, Ca, Fe, K, Mg, Mn, and Na) and DRP measured in porewater in samples collected in August 2004 using Statgraphics (Statgraphics, 2002). Unless indicated, statistical results were significant at the *P* < 0.05 confidence level.

Results and Discussion

Soil Column Experiments

The response of porewater DRP concentrations to the water level treatments were very different for the North site compared to the South site soil columns, suggesting differences in controls on P solubility (Fig. 3). Cores from the South site displayed no significant differences in porewater DRP due to water level or sampling position (i.e., Bottom vs. Top port), and mean DRP concentrations were <0.20 mg L⁻¹ (Fig. 3a). In contrast, porewater from the North site soil cores had DRP levels 10 to 100 times greater than South site (Fig. 3c-d). Levels of DRP in the North site columns tended to be higher in the Bottom compared to the Top sampling port (Fig. 3c-d), a pattern which was not observed in the South site columns. In the South columns, initial samples had the highest DRP followed by a rapid decline over the next few days (Fig. 3a). In the North columns, the lowest DRP levels were observed for the initial samples followed by an increase for 10 to 30 d, and then by a gradual decline.

The DRP in the North columns during Phase I also showed a small response to 19.7 mm of water added at Week 3 (Fig. 3c). This addition of water (corresponding to arrow 1 in Fig. 3c) was followed by an increase in DRP concentration in the Bottom port of the Low water level treatment that continued for 7 d. However, a similar water input at Week 8 (arrow 2 in Fig. 3c), which was drawn down completely in one sampling event 7 d later, had no apparent effect on DRP.

Differences in Fe²⁺ concentrations between North and South site were also observed, especially with the High water level treatments. In the South columns, Fe²⁺ levels in the Top ports attained maximum concentrations of approximately 6.5 mg L⁻¹ compared to 40 mg L⁻¹, for the North columns during Phase I (Fig. 3b,d). The Bottom Port under the High water treatment the South columns had Fe²⁺ as high as 40 mg L⁻¹ in contrast to the North columns with Fe²⁺ concentrations as high as 80 mg L⁻¹.

The response of DRP to increasing water table height in the North site is clearly shown by the DRP response after water was added to the Low water column at the beginning of Phase II. Phase II began at Day 70 (arrow 3 in Fig. 3) when the water table in the Low columns was raised to the same level as in the High water column. The DRP in the Bottom Port increased from 3 to 8 mg L⁻¹ and in the Top port from <1 to 8 mg L⁻¹. Levels of Fe²⁺ also increased. This large increase in DRP contrasts with the High and Intermediate water level treatments (where water levels remained static during Phase II). In these treatments, DRP generally continued a decline that began during Phase I. This is most apparent for the Bottom ports (Fig. 3c,d).

Linear regression showed that Fe²⁺ concentrations were correlated with DRP for the North columns. When the data for Phases I and II were combined, DRP was positively correlat-

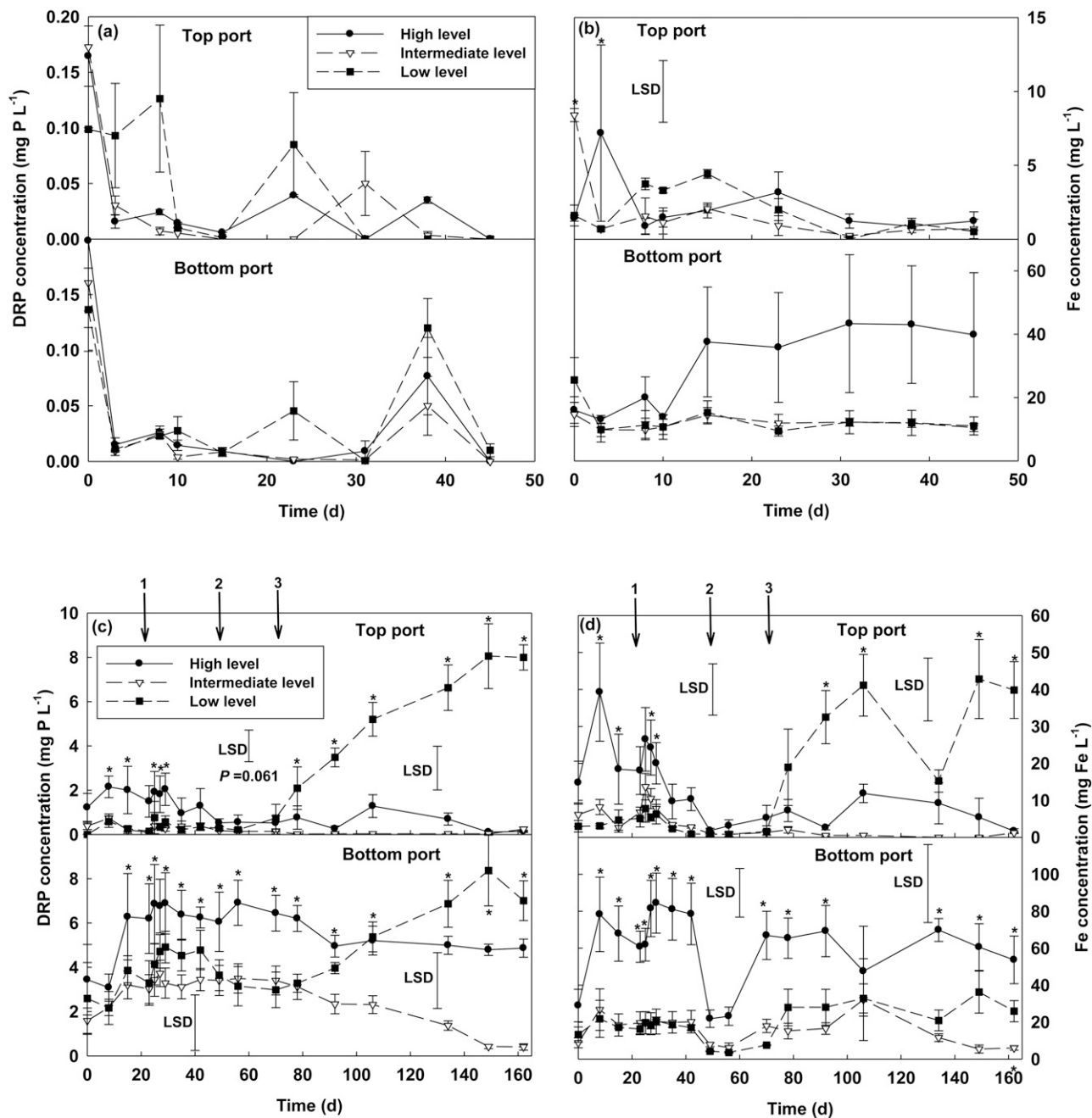


Fig. 3. Trends of (a,c) dissolved reactive phosphorus (DRP) and (b,d) soluble iron (Fe^{2+}) in water samples from the Top and Bottom sampling ports in the South (a,b) and North (c,d) site soil column experiments. Vertical arrows (1) and (2) in (c) and (d) indicate timing of larger (20-mm) water inputs. Vertical arrow (3) indicates start of Phase II, where water level in the Low level treatment was raised to the High level position. Mean values ($n = 3$) are plotted with associated standard error bars. Asterisks indicate significant differences ($P < 0.05$, except where indicated). Stand-alone bars indicate least significant difference (LSD) values for entire data sets where significant differences occurred. Separate LSD values are shown for Phases I and II.

ed ($P < 0.001$) with Fe^{2+} in the Low ($r^2 = 0.58$), Intermediate ($r^2 = 0.57$), and High ($r^2 = 0.62$) treatments. The DRP also showed a strong negative relationship with Eh ($r^2 = 0.75$) in the Low water level treatment. This relationship was influenced by the large decrease in Eh that occurred after the water table was raised to initiate Phase II. The behavior of DRP and Fe^{2+} in the North columns is consistent with sorption of phosphate ions by Fe^{3+} oxyhydroxides during drainage and release of DRP when the Fe oxyhydroxide phase is reduced to soluble Fe^{2+} under com-

pletely saturated conditions (Patrick and Khalid, 1974; de Mello et al., 1998). However, in the South columns, the Fe^{2+} and Eh were not correlated with DRP, suggesting that Fe chemistry was not as important a factor controlling P chemistry in these soils.

Levels of porewater DOC tended to be higher in the North soil columns compared to the South for the Intermediate and High level treatments (Bottom port, Table 3) which is consistent with the higher organic matter in the North soils (Table 1). In the North soil columns, DOC levels in the Bottom ports also

Table 3. Dissolved organic carbon (DOC), pH, and redox potential in Bottom, Intermediate, and Top sampling ports in column experiments using soil from South (S) and North (N) sites maintained at Low (L), Intermediate (I), and High (H) water levels. Mean values across all measurements are shown (with standard deviation).

Site	Water level	Phase	DOC		pH		Redox potential		
			Bottom port	Top port	Bottom port	Top port	Bottom port	Middle port	Top port
			mg L ⁻¹				mV		
S	L	n/a	58.2 (56.8)	9.64 (3.92)	6.78 (0.14)	7.23 (0.13)	-261 (8.53)	-62.4 (64.9)	202 (7.34)
	I		39.6 (16.4)	24.3 (21.1)	6.81 (0.11)	7.33 (0.17)	-186 (42.0)	-6.91 (140)	271 (63.9)
	H		65.8 (41.4)	29.2 (23.1)	6.84 (0.17)	7.52 (0.21)	-198 (12.8)	-166 (57.1)	-191 (42.6)
N	L	I	57.9 (13.7)	24.3 (9.76)	6.65 (0.32)	7.04 (1.34)	69.0 (133)	181 (41)	187 (11.7)
	I		107 (21.5)	23.4 (5.98)	6.54 (0.03)	6.85 (0.21)	-204 (68.9)	-212 (46.8)	152 (17.9)
	H		100 (23.6)	18.6 (5.79)	6.49 (0.02)	6.93 (0.33)	-138 (97.3)	-61.0 (53.3)	-130 (43.4)
	L	II	not determined				-76.7 (38.8)	-152 (8.34)	-119 (26)
	I						-65.4 (103)	15.9 (119)	187 (16.7)
	H						-39.8 (18.1)	-53.7 (16.7)	-177 (46.1)

tended to be higher in the Intermediate and High level treatments compared to the Low level treatment (Table 3), suggesting that DOC was released with reduction of Fe³⁺ oxyhydroxides to Fe²⁺ (Baohua et al., 1994). Porewater pH in both soils was consistently higher in the Top compared to the Bottom sampling port (Table 3), which may have been caused by higher CO₂ partial pressure at greater depth due to microbial respiration (Oren and Steinberger, 2008). In North site soils, DRP was negatively correlated with pH in the Low, Intermediate, and High level treatments ($r^2 = 0.27, 0.39$ and 0.52 , respectively). The DRP was not correlated with pH for the South columns.

Field Porewater Chemistry

Within each sampling location (i.e., North, South, East, and West), porewater data displayed no trends with respect to spatial position (i.e., distance from the ditch), so individual porewater sampler locations were treated as replicates for each site. Porewater DRP concentrations at the North site were substantially higher than the other sites for most sampling periods and depths, although water table levels were similar for both North and South sites for both years (Fig. 4). In 2004, the overall mean DRP concentration at the North site (2.1 mg L⁻¹) was nearly 10-times greater than at the South site (0.29 mg L⁻¹). In 2005, the difference in means was smaller (North = 0.95 mg L⁻¹, South = 0.20 mg L⁻¹). In 2004, DRP tended to increase with depth over the upper 0.21 m, while the trend with depth was not as consistent in 2005 (Fig. 4). Porewater DRP levels at the East and West locations were less than at the North site in 2005. However, it is important to point out that even in the South, East, and West locations, porewater DRP frequently exceeded the swimmable waters standard of 30 µg P L⁻¹ (i.e., 0.03 mg P L⁻¹) (NRCS, 2007). In the North in situ porewater measurements, this standard was frequently exceeded by a factor of 50 or more.

Differences in DRP in the North vs. the South sites at depths of 0.14 m or greater is consistent with the differences observed in the Bottom ports during Phase I in the column experiments (Fig. 3, 4). Also, differences in DRP concentrations between the 0 and 0.2-m depths at the North site in 2004 (2–3 mg L⁻¹) were similar to differences in DRP between the Top and Bottom sampling ports in the Low water level treat-

ment for the North site column (Fig. 3c). However, the in situ North DRP concentrations at depths >0.20 m were less than observed in the Bottom ports of the columns. This might be due to root uptake of DRP by the predominant cattail vegetation (Boers and Zedler, 2008).

Porewater samples from August 2004, which were analyzed for total elemental composition of a range of metals showed that the predominant cations were Ca, Fe, and Mg, with Mn present at lower concentrations (Fig. 5). Similar to DRP, cation concentrations generally increased with depth to about 0.2 m. The decrease in pH with depth is similar to what was observed in the columns experiments (Table 3). The Fe concentrations below 0.2 m were similar to concentrations observed in the Bottom port of the columns with High water level during Phase I (Fig. 3). Porewater DRP was positively correlated with Fe, Mn, and Ca, and negatively correlated with pH (Table 4). The strength of the correlations was consistently greater in the upper 0.14 m where the greater differences were observed compared to the entire 0.49 m.

The redox sensitive ions Fe²⁺ and Mn²⁺ showed much greater change in concentration from the surface to depths of 0.14 m or greater, compared to Ca²⁺ and Mg²⁺ which do not undergo oxidation and reduction in soils (McBride, 1994) (Fig. 5). Concentrations of Mg²⁺ and Fe²⁺ were similar at the 0.14-m depth, but at the surface Mg²⁺ levels were greater than Fe²⁺. The low concentrations of Fe²⁺ and Mn²⁺ at the surface are indicative of higher redox status and greater stability of insoluble Fe(III) oxyhydroxides and Mn(IV) oxides above the water table (Fig. 4), where gas exchange with the air is greatest and redox potential is the highest. This is similar to the lower Fe concentration in the Top sampling ports compared to the Bottom port in the North column experiment. Changes in P concentration with depth were more similar to Mn and Fe than Ca and Mg, at depths <0.2 m (Fig. 5).

The increase in Ca²⁺ and Mg²⁺ concentration with depth can be attributed to two factors. As Fe (III) oxyhydroxides in soils undergo reduction, some of the Fe²⁺ displaces Mg²⁺ and Ca²⁺ from cation exchange sites (Boivin et al., 2002). In addition, the decrease in exchange of soil gases with the air as soil moisture saturation increases results in higher partial pressures of CO₂ and higher concentration of carbonic acid in soil solutions, leading to H⁺ displacement of Ca²⁺ and Mg²⁺ from ion exchange sites (Inskeep and Bloom, 1986; Bloom, 1999).

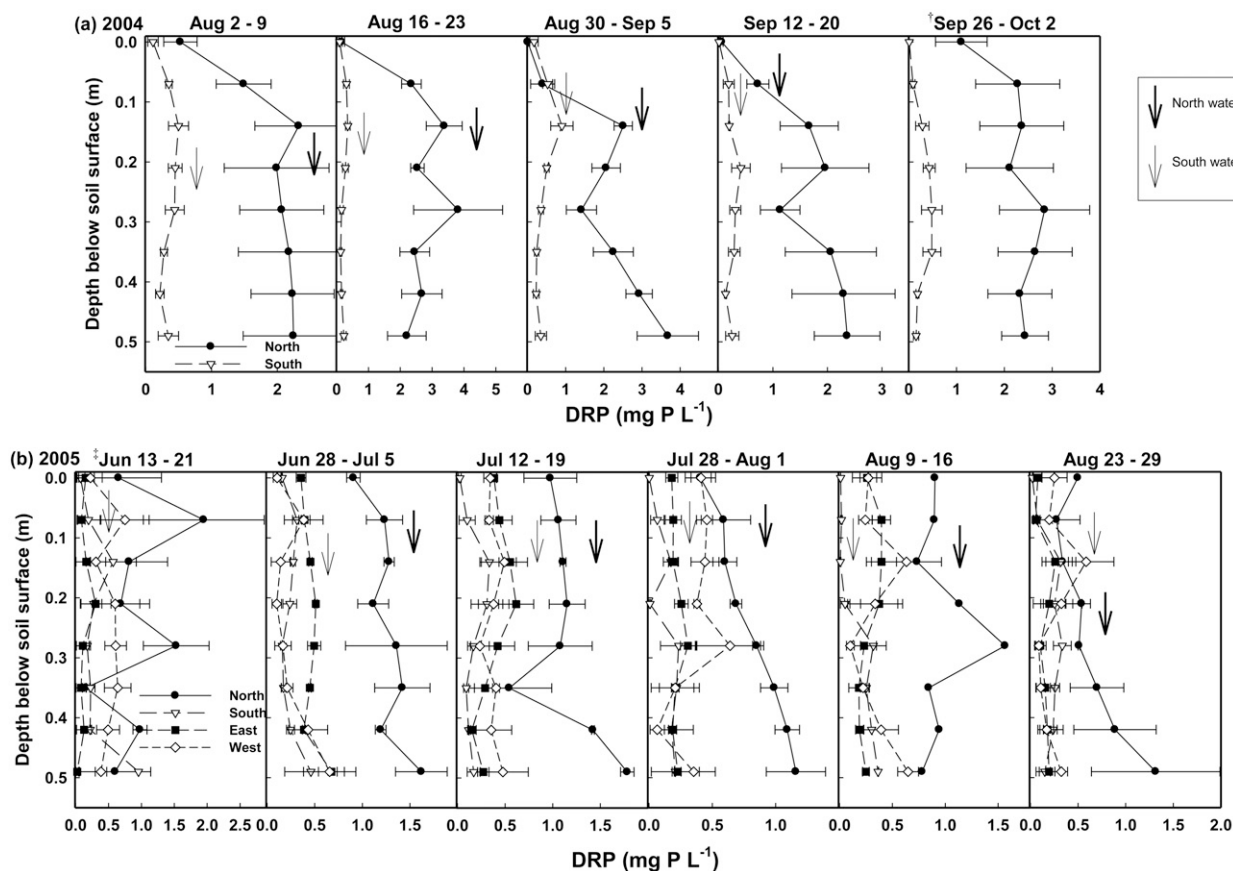


Fig. 4. Vertical profiles (relative to the soil surface) of dissolved reactive phosphorus (DRP) concentration in samples collected from four field locations in Rice Lake Wetland during (a) 2004 and (b) 2005. Mean values ($n = 3$) are plotted with standard error bars. Water table depth at time of sampling is indicated by arrows. †For Sep 26 through Oct 2, South water table was 0.13 m above the soil surface, and North water table was 0.03 m below the surface. ‡For June 13 through June 21, North water table was 0.01 m above the soil surface.

Controls over Phosphorus Release

North site soils contained about twice as much total P but substantially less calcium carbonate (CaCO_3) equivalents (CCE) than South site soils (Table 1). These differences are reflected in a 10-fold lower CCE/P mass ratio in North ($150 \text{ g CCE g}^{-1} \text{ P}$) compared to South ($1500 \text{ g CCE g}^{-1} \text{ P}$) site soils. While there is no direct evidence regarding mechanism, the much higher CCE/P ratio in the South site soils suggests that P adsorption and occlusion by CaCO_3 may have been more important in controlling DRP levels in the South site than the North. In contrast, adsorption and occlusion of P in Fe-oxyhydroxides is the primary control of DRP at the North site. This hypothesis is consistent with the increased DRP and Fe^{2+} release on flooding in the soil column experiment (Fig. 3 c-d), positive DRP-Fe correlations and negative DRP-Eh correlations in the soil column experiment, as well as the positive DRP-Fe correlations in field porewater (Table 4). These trends all suggest that microbially-mediated reduction of Fe^{3+} to Fe^{2+} under low Eh conditions, with concomitant release of Fe-bound P, was an important control over DRP levels in the North site soils (Moore and Reddy, 1994). While the South soil columns did

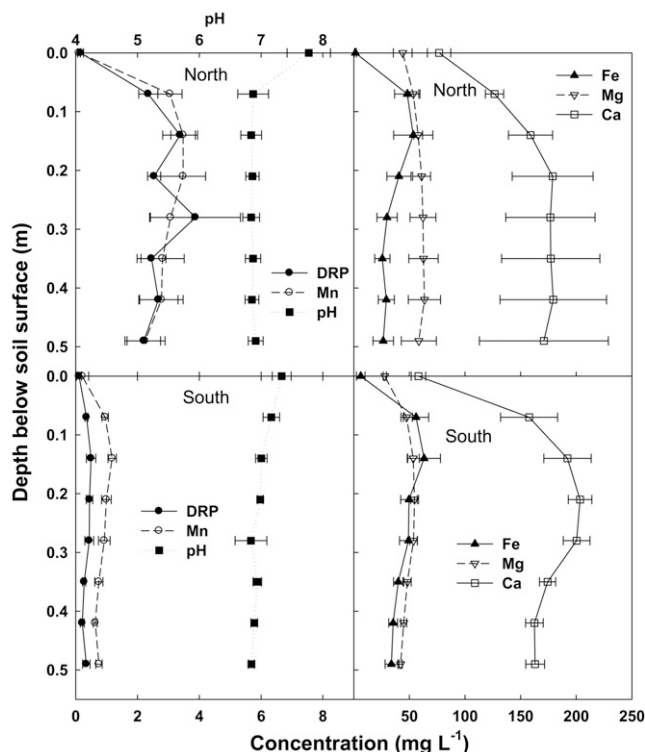


Fig. 5 (right). Vertical profiles of dissolved cations and pH in samples collected August 2004 from the North site (upper graphs) and South site (lower graphs).

Table 4. Results of regression analysis of dissolved reactive phosphorus (DRP) with porewater data for field porewater samples collected in August 2004.

Site	Depth	Pearson's correlation coefficient (<i>r</i>)				
		pH	Fe	Mn	Ca	Mg
	m					
N	0–0.49†	–0.70***	0.39*	0.60***	0.09	0.14
	0–0.14‡	–0.78**	0.74*	0.99***	0.72*	0.32
S	0–0.49†	–0.37*	0.52***	0.55***	0.34*	0.23
	0–0.14‡	–0.79**	0.62*	0.88***	0.71*	0.74*

* $P < 0.05$.

** $P < 0.01$.

*** $P < 0.001$.

† Analyses done on entire data set.

‡ Analyses done only on data collected from upper 0.14 m.

not exhibit P release on flooding and field porewater DRP levels were much lower in the South, the positive in situ porewater DRP-Fe correlations suggest Fe-P reactions also played a role in the South site to some extent. The strongly positive DRP-Mn correlations in porewater at both sites (Table 4) also suggests that analogous processes involving Mn reduction with P release were at play in both soils, as also found by Moore and Reddy (1994). However, low molar Mn-Fe ratios in both the North (0.06–0.11) and South (0.02–0.03) suggest that sorption involving Mn was less important relative to Fe-bound P.

Concentrations of Mg were also positively correlated with DRP in single-factor analysis in the upper 0.14 m in the South site (Table 4). This correlation most likely reflects the fact that, under these conditions, Mg tends to co-precipitate in calcite structures. Ratios of Mg/Ca were generally less than 1:3 (Fig. 5). Due to its high solubility, Mg carbonate is not likely to be directly involved in controlling P solubility (McBride, 1994). Magnesium (like Ca) is correlated with P because the high water level displaces Mg (and Ca) from exchanges sites due to increased carbonic acid and increased Fe^{2+} (Boivin et al., 2002; Inskeep and Bloom, 1986). But there is no evidence that this correlation represents a causative relationship between Mg^{2+} and DRP release.

Olila and Reddy (1997) also showed that highly calcareous lake sediments can release P under low-Eh conditions in the presence of sufficient Fe oxyhydroxide. In calcareous sediments with lower Fe, Olila and Reddy (1997) found little response of DRP to moderate changes in Eh. Draining for a period of time followed by flooding can result in mobilization of P in plant detritus (Pant and Reddy, 2001), and the released P can sorb on soil Fe oxyhydroxides. The expected response on flooding (provided sufficient Fe oxyhydroxide) is an increase in DRP (Olila et al., 1997; Venterink et al., 2002). Shenker et al. (2005) studied the response of calcareous peat soils that had been previously drained for agriculture and fertilized to Olsen soil test P values of 50 to 80 mg kg^{-1} . Upon flooding in laboratory columns, P sorbed by Fe oxyhydroxide was released as DRP, which reached concentrations of 6 to 12 mg L^{-1} , similar to the levels observed here (Fig. 3c). Shenker et al. (2005) also observed Fe^{2+} concentrations of 30 to 50 mg L^{-1} after 120 d of flooding, similar to the current results (Fig. 3d). Surridge et al. (2007) flooded columns of riverine flood plain peat soil in

the laboratory for 43 d and observed that porewater DRP was highly correlated with Fe^{2+} . They measured concentrations of DRP as high as 3.0 mg L^{-1} in the porewater and found that the DRP diffused into the floodwater resulting in concentrations as high as 0.8 mg L^{-1} . This demonstrates that the soils like those in our study, especially the North site soil, have the potential to have a negative impact on water quality on flooding.

Our experiment using soils from the North site was also designed to examine the effects of flooding following extended periods of drainage on P release in the Low level treatment (i.e., Phase I compared to Phase II). The subsequent release of P during Phase II was similar in magnitude to that occurring in the High water level columns (Fig. 3c). Thus, these data provide no evidence that the period of drainage stimulated additional P release due to mineralization as was originally hypothesized by NRCS (NRCS, 2007). Flooding followed by drying has been shown to increase P sorption compared to continuously dry soils by increasing levels of amorphous Fe oxyhydroxides (Sah and Mikkelsen, 1986). The Fe oxyhydroxides would be expected to sorb P mineralized from organic matter, which could be released on reflooding. However, it is possible that the duration of the experiments was not sufficient to observe these effects, or that soils in this study were not allowed to dry to a sufficient extent, that is, humid atmospheric conditions were maintained during the incubation.

Greenhouse Gas Fluxes

The North Intermediate treatment had lower N_2O flux and higher CH_4 flux compared to the South Intermediate treatment (Fig. 6), which is consistent with the lower Eh levels observed in the North (Table 3). However, in general, greenhouse gas fluxes displayed similar patterns in both soil column experiments (Fig. 6). Similar to other studies (Regina et al., 1999; Freeman et al., 1997), higher water level and accompanying lower Eh were associated with lower N_2O fluxes, but higher CH_4 fluxes (Altort and Mitsch, 2008; Fiedler and Sommer, 2000; Kelly et al., 1997). Fluxes of CO_2 generally did not differ among treatments. After converting to CO_2 equivalents and summing together the individual gas fluxes, the High water level treatment with both the North and South site soils emitted the greatest amount of total greenhouse gas (Fig. 6 and 7). Thus, the increase in emissions of CH_4 (GWP = 23 times greater than CO_2) more than compensated for the decrease in emissions of N_2O (GWP = 300 times greater than CO_2) (Forster et al., 2007). In the Low level treatments, N_2O and CH_4 contributed similar amounts to the total GWP (9–20%) (Fig. 7). The proportion of total GWP contributed by N_2O decreased from 14% to $\leq 1\%$ as water level was raised, while the proportion contributed by CH_4 increased from 9 to 20% to 60 to 80% (Fig. 7).

The observed N_2O fluxes were in the same range as those measured in incubated cores from natural and drained noncalcareous peatlands in Finland (Regina et al., 1999). Fluxes of N_2O in the High water level treatment were also similar to cumulative measurements in a water treatment wetland in Wales (Freeman et al., 1997). This suggests that more reducing conditions may have favored greater reduction of N_2O to N_2 and/or

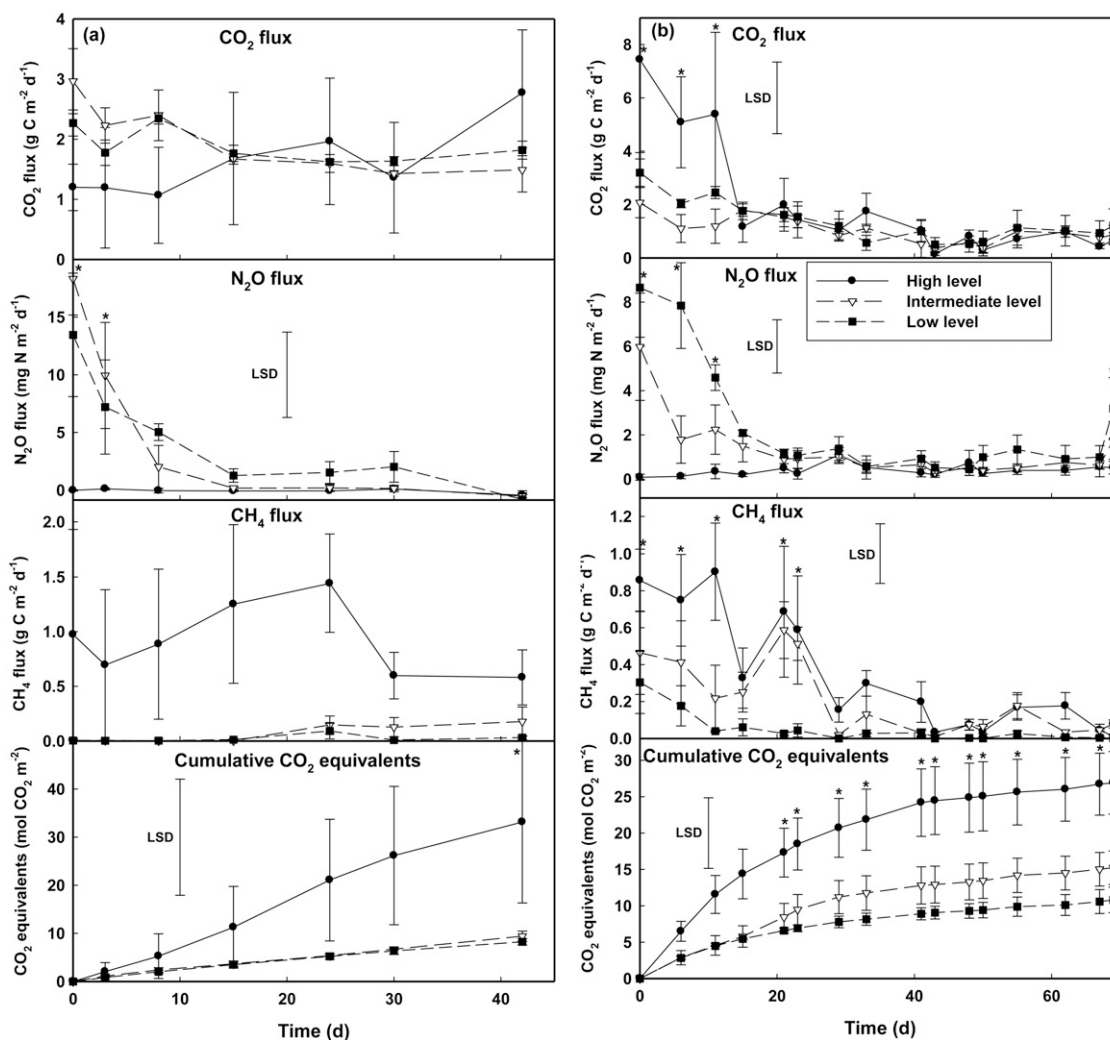


Fig. 6. Fluxes of carbon dioxide (CO₂), nitrous oxide (N₂O), methane (CH₄) and cumulative CO₂ equivalents vs. time in column experiments using soils from the (a) South and (b) North sites (Phase I only). Mean values ($n = 3$) are plotted with standard error bars. Least significant difference (LSD) values are shown for data sets where significant differences occurred. Asterisks indicate significant differences ($P < 0.05$).

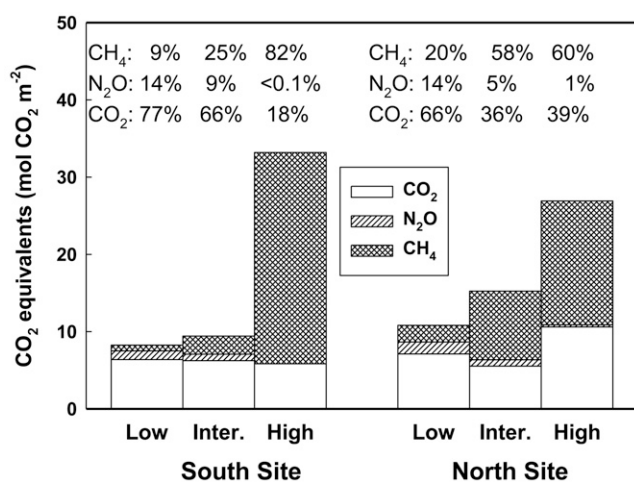


Fig. 7. Individual contributions of carbon dioxide (CO₂), nitrous oxide (N₂O), methane (CH₄) to the total cumulative greenhouse gas emissions in the soil column experiments. Bars represent mean values ($n = 3$). Percentages above each bar are contributions of each gas to the total. Significant differences in total CO₂ equivalents are indicated in Fig. 6.

constrained denitrification due to limiting levels of nitrification-generated nitrate resulting from low oxygen availability (Regina et al., 1999). Before beginning the North site column experiment, initial porewater nitrate levels were 0.38 (0.01) mg N L⁻¹ and 0.33 (0.02) mg N L⁻¹ in the 0 to 0.1 m and 0.1 to 0.2 m depths, respectively. Porewater NO₃⁻ concentrations on Day 57 were higher: 5.4 (1.5), 1.5 (0.52), and 1.6 (0.56) mg N L⁻¹ for the Low, Intermediate, and High water level treatments, respectively, indicating that nitrification (and possibly N mineralization) had occurred. The trend in NO₃⁻ by treatment (i.e., higher NO₃⁻ in the more highly drained treatments) is consistent with greater rates of nitrification (and possibly mineralization) occurring under more highly drained conditions, which is expected since nitrification is an aerobic process (Prosser, 1989).

Our findings are consistent with previous work showing that higher water levels in wetland soils increase methane release (Altor and Mitsch, 2008; Fiedler and Sommer, 2000; Kelly et al., 1997). The observed CH₄ fluxes were generally higher than measurements in a Canada fen soil (Moore and Knowles, 1989), an Alaska peat bog (Moosavi et al., 1996),

and a temperate lake marsh (Fiedler and Sommer, 2000). These data emphasize the importance of accounting for CH₄ in determining the GHG budget of temperate wetlands.

Fluxes of CO₂ generally did not differ among treatments, except during the first 2 wk in the North site soil (Fig. 6b). Unlike previous studies (Moore and Knowles, 1989; Smith et al., 2003; DeBusk and Reddy, 2001), water level had little or no effect on CO₂ release in this study. We observed a significant positive correlation between daily fluxes of CO₂ and CH₄ in the North ($r^2 = 0.67$) and South ($r^2 = 0.32$) site experiments. This may be explained by CH₄ oxidation occurring in the upper, less-reduced part of the soil columns. Aerobic conditions support methanotrophs, provided an adequate supply of CH₄ exists (Harriss et al., 1982; Happell and Chanton, 1993).

It is important to point out that the GHG budget of any ecosystem must account for CO₂ fixed by vegetation during the growing season, and that our laboratory measurements obviously did not account for this component. Thus, under actual field conditions, the contribution of CO₂ to the total shown in Fig. 7 would be decreased due to photosynthetic uptake of the vegetation. Another important limitation of the laboratory study is related to the fact that emergent macrophytic vegetation, including *Typha latifolia*, promote gas exchange between the atmosphere and subsurface via aerenchyma (Schutz et al., 1991). This mechanism, which was also not accounted for in the lab experiments, can transport oxygen from the atmosphere to the rhizosphere, and/or transport gases (N₂O, CH₄, CO₂) from the rhizosphere to the atmosphere. Studies have shown that aerenchyma can be the primary mechanism of CH₄ transport in vegetated wetlands (Van der Nat and Middelburg, 1998). Thus, in situ measurements are required to obtain more accurate estimates of the actual GHG budgets of the Rice Lake wetland.

Conclusions

The laboratory column study and in situ monitoring provide evidence that increasing water levels result in increased porewater DRP concentrations, especially at the site located in the northern part of Rice Lake Wetland. The dominant process in these soils was release of DRP from Fe oxyhydroxides that follows reduction to Fe²⁺ and the porewater data show that DRP can attain concentrations in excess of 1 mg L⁻¹. In the soil from the southern part of the wetland, where total soil P is less and CaCO₃ is more dominant, reduction of Fe oxyhydroxides may contribute to DRP, but the decrease in pH due to the increase in partial pressure of CO₂ in saturated soil also may contribute to release of carbonate-bound P. However, in this soil the porewater DRP is much less than in the soil from the northern part of the wetland. These results provide support of the hypothesis that flooding has the potential to release DRP to the floodwater, and any change in management plan that involves flooding must consider this potential, especially for the northern part of the wetland.

The GHG data from the soil columns show no differences in greenhouse gas in different parts of the wetland. Higher water levels in the soil cores from both the North and South sites resulted in decreased N₂O emissions but increased CH₄ emissions. The in-

crease in CH₄ more than compensated for the decreased N₂O, resulting in higher net total global warming potential at higher water levels. Raising the wetland water table has the potential to increase both DRP levels and greenhouse gas emissions, complicating the overall cost-to-benefit analysis of such restoration.

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